Chapter 1: Background and introduction to cobalt tris(phosphino)borate chemistry

1.1 Introduction

Threefold symmetry is a successful design strategy for a myriad of inorganic transition metal complexes, in part because three-coordinate complexes in threefold symmetry have a site open for reactions (Figure 1.1). Many key advances have been achieved using this template, including the activation of dinitrogen and other small molecules.[1] Threefold symmetric complexes are particularly adept at stabilizing metal-ligand triple bonds. Since species that can be assigned to the C_{3v} point group (or higher symmetry with a threefold axis) have a set of orbitals of *e* symmetry, two energetically equivalent π-bonds can be formed. Some examples of C_{3v} pseudotetrahedral complexes with metal-ligand triple bonds are shown in Figure 1.2.[2] These complexes can contain three equivalent monodentate ligands[3] or a single tripodal ligand.[4] While d^0 and d^2 metal-ligand multiple bonds are ubiquitous, examples with higher electron counts are rare; however, this field of research has recently seen considerable growth.[5]

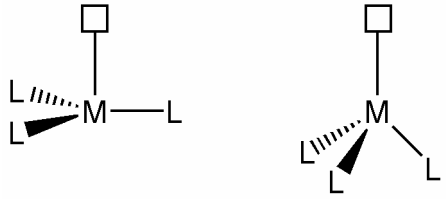

Figure 1.1. Two examples of threefold symmetric complexes with an available reaction site (□).

Many neutral and anionic tridentate ligands have been designed to take advantage of threefold symmetry in order to achieve *facial* coordination about a pseudotetrahedral metal complex. The tris(pyrazolyl)borates are among the most prominent anionic

ligands.[6] Neutral tripodal phosphine ligands, such as triphos (triphos = $H_3CC(CH_2PPh_2)_3$), have also been developed.[7] These and other prominent tridentate ligands are shown in Figure 1.3.

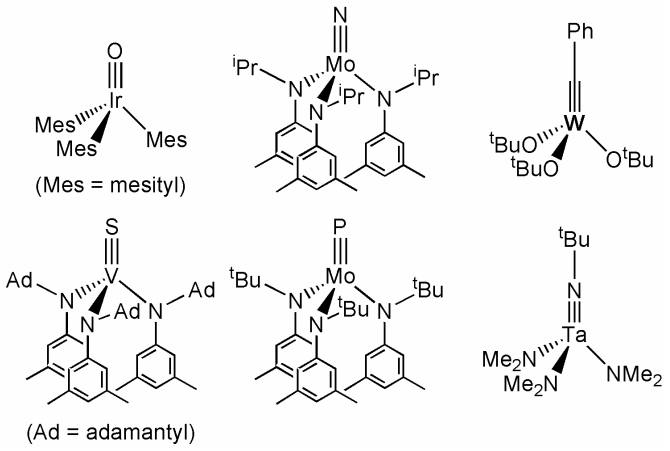

Figure 1.2. Some examples of metal-ligand triple bonds in threefold symmetry. See reference 2 for details.

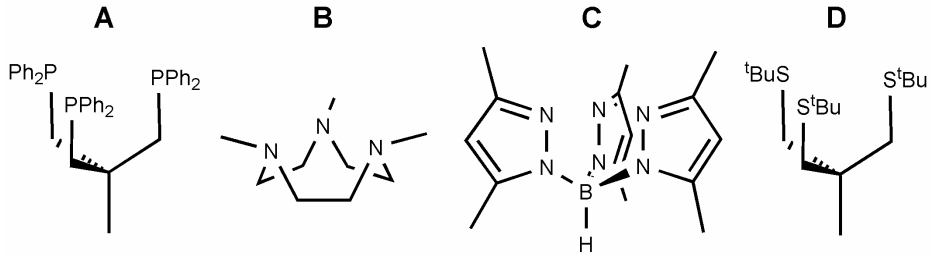

Figure 1.3. Prominent tridentate ligands that align in a *fac* arrangement on a metal center: (A) triphos ($H_3CC(CH_2PPh_2)_3$), (B) Me_3-tacn (1,4,7-trimethyl-1,4,7-triazocyclononane), (C) $Tp^{3,5\text{-}Me2}$ hydro-tris(3,5-dimethyl-pyrazolyl)borate, and (D) [$Tt^{tert\text{-}butyl}$] ([$PhB(CH_2S^tBu)_3$]$^-$).

1.2 Design of new tripodal anionic phosphine ligands

Phosphines are among the most ubiquitous ligands in transition metal chemistry, and their importance in catalysis has been well-documented.[8] Anionic monodentate and, to a more limited extent, bidentate phosphine ligands have also been prepared.[9] Many of these species incorporate a borate anion within the ligand backbone. Tripodal ligands incorporating a borate anion in the ligand backbone are well-established for nitrogen[10] and sulfur[11] donors (Figure 1.3), but there were no examples of anionic tridentate phosphorus ligands until the recent synthesis of a new class of tripodal anionic phosphines, [$PhBP_3$] ([$PhBP_3$] = [$PhB(CH_2PPh_2)_3]^-$) and [$PhBP^{iPr}_3$] ([$PhBP^{iPr}_3$] = [$PhB(CH_2P^iPr_2)_3]^-$).[12] These ligands have opened up new frontiers in synthesis (Figure 1.4), as the incorporation of an anionic charge into the ligand framework effectively makes these species more electron-releasing than their neutral analogs, such as triphos.[13] These six electron donor ligands (L_3) are isolobal to tris(pyrazolyl)borates ([Tp]) and the well-known cyclopendienyl ([Cp] = cyclopendienyl) ligands. This similarity to [Tp] and [Cp] suggests that it should be possible to prepare isoelectronic complexes that incorporating phosphine donors.

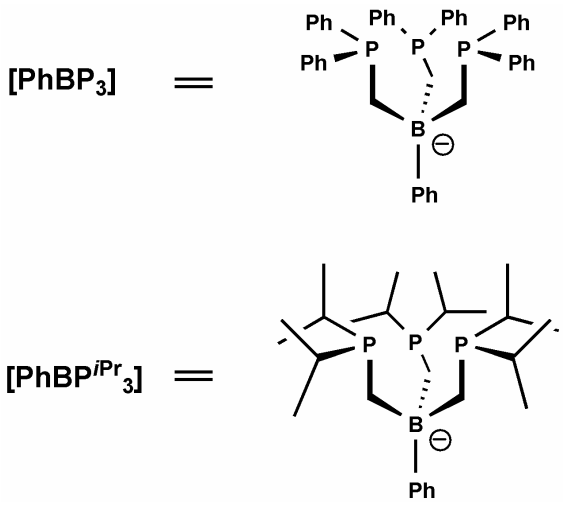

Figure 1.4. Chemical structures of [$PhBP_3$] and [$PhBP^{iPr}_3$].

1.3 Cobalt tris(phosphino)borate chemistry

Given the isolobal analogy between [$PhBP_3$] and [Cp] and [Tp] ligands, four-coordinate species featuring "[$PhBP_3$]CoX" can be expected to have the molecular orbital diagram shown in Figure 1.5, depending on the oxidation state of the metal center. This predicted molecular orbital diagram shows that Co(II) complexes would be high spin similar to ones previously prepared with "tetrahedral enforcer" ligands such as [Tp]. What became immediately apparent upon experimental investigation of [$PhBP_3$]Co-X complexes is that this molecular orbital diagram is incorrect. The Co(II) complexes obtained were not high spin (S = 3/2), but were in fact *low spin* (S = ½). This result was unexpected and unprecedented. Pseudotetrahedral Co(II) species were previously held to be always high spin with classic "three over two" splitting diagrams as derived from Ligand Field Theory.[14] Moreover, pseudotetrahedral Co(II) centers are generally assumed to adopt high spin arrangements within metalloenzymes.[15] The experimental data led to the establishment of a new molecular orbital diagram, shown in Figure 1.6, in order to explain these results. In the new interpretation, the C_{3v} symmetric manifold

undergoes an axial distortion away from the idealized tetrahedral geometry resulting in a new orbital diagram, which places the a_1 orbital at a much lower energy. This molecular orbital depiction is now reminiscent of octahedral coordination, as though the tridentate ancillary [$PhBP_3$] ligand occupies three *facial* sites of an octahedron with the fourth ligand occupying the vacant position opposite. The reasons for this low spin ground state will be discussed in additional detail in Chapter 3 (vide infra).

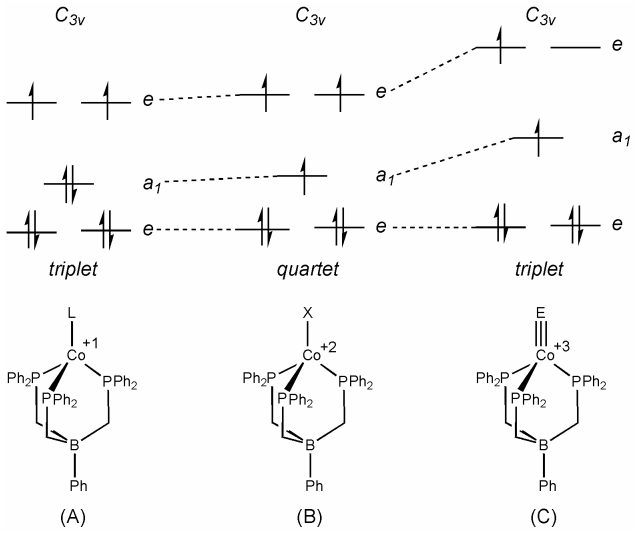

Figure 1.5. Qualitative splitting diagram assuming approximate C_{3v} symmetry for the frontier orbitals of (A) [$PhBP_3$]Co-L; (B) [$PhBP_3$]Co-X; and (C) [$PhBP_3$]Co≡E. The relative orbital energies are not accurately known.

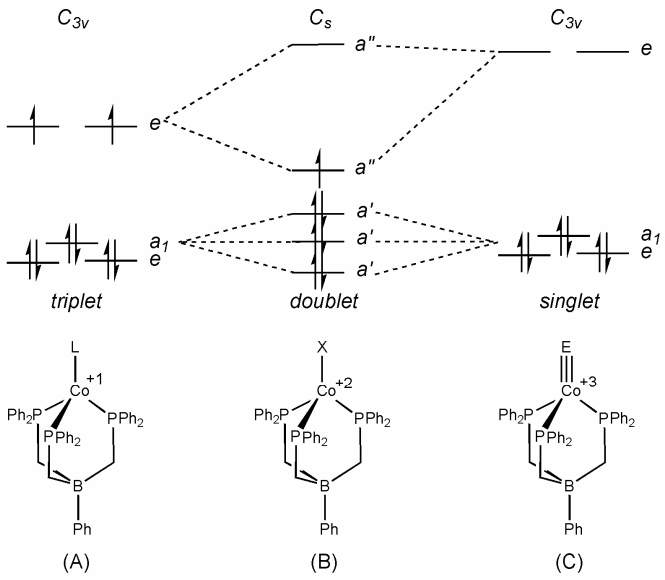

Figure 1.6. Qualitative splitting diagram assuming approximate C_{3v} or C_s symmetry for the frontier orbitals of (A) [$PhBP_3$]Co-L; (B) Jahn-Teller distorted low spin [$PhBP_3$]Co-X; and (C) [$PhBP_3$]Co≡E. The relative orbital energies are not accurately known.

Two hypotheses can be derived from the proposed new molecular orbital diagram shown in Figure 1.6. First, this diagram implies that it may be possible to stabilize a high spin species with the same tripodal ligand if the spin states of low and high spin Co(II) complexes are close in energy. This finding could lead to the preparation of four-coordinate spin crossover complexes. Although a limited number of five-coordinate spin crossover complexes have been prepared,[16] most Co(II) spin crossover complexes are six-coordinate;[17] no example of a four-coordinate spin crossover species had been established on any transition metal. In addition, the diagram suggests that the presence of strong donor ligands, combined with a threefold symmetry about the metal center, may allow for the stabilization of Co(III) metal-ligand triple bond. Excluding Fischer-type carbenes,[18] no cobalt-heteroatom multiple bond had previously been reported.

Bergman's imide, [Cp*]Ir≡N^{t}Bu ([Cp*] = pentamethyl-cyclopentadienyl) is a rare example of a group nine metal-ligand multiple bond.[19] An isolobal imido complex such as [$PhBP_3$]Co≡NR (R = alkyl or aryl) could be prepared employing [$PhBP_3$] instead of [Cp*] as the auxiliary L_2X ligand, which would give a closed shell 18 electron species.

It is worth asking why the "two over three" molecular orbital diagram is the preferred diagram for pseudotetrahedral complexes supported by [$PhBP_3$]. The d_z^2 (a_1) orbital is stabilized by an axial distortion caused by the narrow P-Co-P angles. Lowering the energy of this orbital allows for the stabilization of low spin Co(II) species as well as stable metal-ligand multiple bonds. A similar argument has been presented to explain the stability of [Cp*]IrN^{t}Bu. The detailed argument for the complexes' stabilization will be provided in Chapter 5.

The following chapters show how a strong anionic phosphine donor ligand that enforces threefold symmetry leads to two unprecedented results: a low spin pseudotetrahedral Co(II) complex and a stable Co(III) imide complex.

1.4 Chapter summaries

This chapter so far has presented the advantages of threefold symmetry from a molecular orbital perspective. Complexes featuring C_{3v} symmetry can form two equivalent π-bonds between a metal and a ligand, giving rise to stable metal-ligand triple bonds. Several tripodal L_2X type donor ligands, such as [Tp], are presented and compared to the new ligand [$PhBP_3$]. Experimental observations, which are presented in greater detail in the following chapters, show that the pseudotetrahedral Co(II) species can adopt a low spin rather than the expected high spin state. The strong electron donation and unusual local coordination geometry stabilizes these low spin species. A

new molecular orbital diagram suggests two hypotheses. First, it may be possible to synthesize an unprecedented pseudotetrahedral spin crossover complex. Second, a Co(III) species may be amenable to the formation of a metal-ligand triple bond. No examples of cobalt-ligand multiple bonds have been prepared previously, excluding Fischer carbenes.

The synthesis of the [$PhBP_3$] ligand is the focus of Chapter 2. While the ligand had been prepared previously as a tin or lithium complex, problems that arise during the attempted metalation onto transition metals have reduced its utility as a synthetic reagent. The preparation of the homoleptic thallium transmetalating reagent [$PhBP_3$]Tl allows for the easy preparation of a variety of late metal [$PhBP_3$] complexes. Furthermore, [$PhBP_3$]Tl is the first example of a stable homoleptic Tl(I) phosphine complex.

The study of [$PhBP_3$]Co-X (X = I, Br, or Cl) is the theme of Chapter 3, which focuses on the novel monomeric low spin pseudotetrahedral complex [$PhBP_3$]CoI. Structural and magnetic studies provide evidence for a low spin ground state, and DFT investigations help explain why this ground state is favorable. The bromide and chloride complexes are discussed in terms of their monomer/dimer equilibria. In addition, a high spin complex featuring the same [$PhBP_3$] ligand scaffold is presented. These complexes are compared structurally and magnetically to several other pseudotetrahedral Co(II) complexes.

Spin state control in pseudotetrahedral Co(II) complexes is the emphasis of Chapter 4. Low spin, spin crossover, and high spin complexes are prepared with a wide variety of X-type ligands following the general formula of [$PhBP_3$]Co-X (X = thiolate, aryloxide, or siloxide). The effects of sterics and electronics are investigated to

determine how each plays a role in determining the spin state of each complex. Structural comparisons show that the complexes can be arranged into two classes: umbrella distorted and off-axis distorted. Additional complexes featuring the more sterically encumbering ligand [$PhBP^{iPr}_3$] are also evaluated.

The preparation of stable cobalt imido complexes ([$PhBP_3$]Co≡NR, R = alkyl or aryl) is the subject of Chapter 5. The synthesis of these species and their structural characterization are described. Several different imido complexes were prepared by two different synthetic routes. In addition, the reactivity of these species is explored. The stabilization of the late-metal metal-ligand multiple bonds is discussed, aided by DFT calculations.

The synthesis and characterization of a bimetallic bridged cobalt nitride complex, ([$PhBP_3$]Co)$_2$(μ-N), is discussed in Chapter 6. This mixed-valent species is the first example of a μ_2-bridging nitride involving cobalt. Since the μ_2-bridging nitride is paramagnetic the nature of the unpaired electron is investigated. Finally, the complex is compared to other μ_2-bridging nitrides of iron.

Attempts to prepare a cobalt carbene from diazoalkanes are covered in Chapter 7. Diazoalkane adducts of "[$PhBP_3$]Co" were prepared and characterized. These species are compared to other late metal diazoalkane complexes as well as the related cobalt imide complexes. Both end-on and side-on diazoalkane species were prepared, making this one of the only systems that supports both diazoalkane bonding modes.

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